STRUCTURAL STUDIES IN MAIN GROUP CHEMISTRY

XI*. TIN-119m MÖSSBAUER INVESTIGATIONS OF TRIORGANOTIN DERIVATIVES OF SUBSTITUTED PYRIDINES

PHILIP G. HARRISON* and ROBIN C. PHILLIPS

Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD (Great Britain)

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Summary

Tin-119m Mössbauer and selected infrared and ^{1}H NMR data are reported for twenty four triorganotin derivatives of substituted pyridines and related ligands, and conclusions concerning structure inferred. Mössbauer quadrupole splittings in the ranges 3.09-3.38 mm sec^{-1} and 2.92-3.22 mm sec^{-1}, respectively, for the 2- and 3-pyridone derivatives indicate five-coordinate *trans*-R$_3$SnX$_2$ trigonal bipyramidal configurations at tin with planar R$_3$Sn moieties. In the case of the derivatives of 2-pyridone, the extra coordination to give linear chain structures arises from bridging oxygen atoms, but bridging via either oxygen or the pyridyl nitrogen atom may occur in the derivatives of 3-pyridone. Similar oxygen-bridged chain structures are also postulated for the triorganotin derivatives of 2-pyridylalcohol and 2-pyridylaldehyde oxime, but lower splitting values of 2.63(5)-2.93 mm sec^{-1} indicate some relaxation from planarity of the R$_3$Sn group towards tetrahedral. The splittings are observed to decrease in the order Me > Et > Pr, illustrating that the deviation from planarity and the bond distance of the coordinate O···Sn bond increase with the steric bulk of R. Much lower splittings of 1.60-2.27 mm sec^{-1} are observed for the derivatives of 2-thiopyridone and 8-hydroxyquinoline, which, with the presence of three tin—carbon stretching modes in the infrared spectrum for the methyltin compounds, are consistent with the alternative five-coordinate *cis*-R$_3$SnX$_2$ geometry at tin. The very high splitting values, together with the low values of the anti-symmetric OCO stretching vibration of the carboxylate group and the multiple tin—carbon stretching modes observed for the methyltin compounds in the infrared, have been interpreted in terms of the six-coordinate *mer*-R$_3$SnX$_3$ stereochemistry for

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* For Part X see ref. 1.

the triorganotin esters of 2-pyridylcarboxylic and 2,6-pyridyldicarboxylic acids. The low and almost constant value of the two-bond coupling constant $^2J(^1H\text{—}C\text{—}^{119}Sn)$ for the methyltin derivatives indicate that in solution either four or five-coordinate cis-R_3SnX_2 structures are adopted.
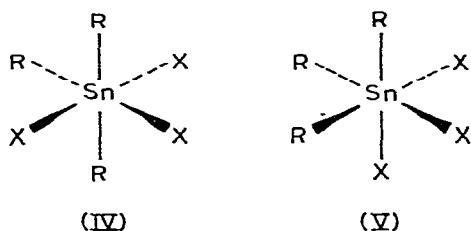
Introduction

It is the convention among chemists, in the absence of unequivocal structural data from X-ray, neutron, or electron diffraction, to infer molecular structure from spectroscopic data. In this context, tin chemistry is rich in applicable techniques; infrared, Raman, ^1H and ^{119}Sn NMR, mass, and ^{119}Sn Mössbauer spectroscopies each having been used with varying degrees of success. The latter has been used to distinguish between cis and trans isomers of octahedrally coordinated diorganotin species [2], but in the case of triorganotin derivatives, where 4-, 5-, and 6-coordination may be possible the situation is far from clear. The bulky triphenylsiloxy group is probably large enough to prohibit intermolecular association in $Me_3SnOSiPh_3$ and $Ph_3SnOSiPh_3$, thus providing examples of four-coordinate triorganotin compounds. The observed quadrupole splittings for the two compounds are 2.09 and 1.86 mm sec^{-1}, respectively [3]. Bancroft [4] has recently described a method to distinguish the three isomers of trigonal bipyramidally-coordinated triorganotin species, the postulated quadrupole splittings ranges being ca. 1.7-2.3 mm sec^{-1} for the cis-isomer I, ca. 3.0-3.9 mm sec^{-1} for the equatorial-isomer II, and ca. 3.5-4.1 mm sec^{-1} for the mer-isomer III.

(I)   (II)   (III)
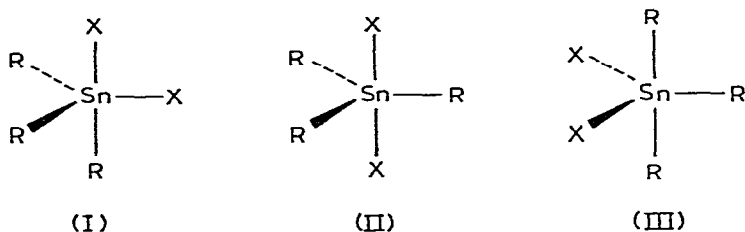
Triorganotin 8-hydroxyquinolates have long been considered to possess structure I albeit without crystallographic confirmation. However, X-ray crystal data are available for N-benzoyl-N-phenyl-O-(triphenylstannyl)hydroxylamine [5] and triphenyltin dibenzoylmethane [6] confirming them as examples of structural type I with measured quadrupole splittings of 1.94 [7] and ca. 2.2 mm sec^{-1} [4], respectively. Crystal data are available for quite a large number of species with the equatorial structure II: with observed quadrupole splittings in parentheses (mm sec^{-1}), Me_3SnF [8] (3.47-3.86) [3], $Me_3SnCl \cdot C_5H_4N$ [9] (3.35-3.52) [3], $Me_3SnCl \cdot Ph_3P=CHCOOMe$ [10] (3.44) [11], Me_3SnNCS [12] (3.67) [3], Me_3SnCN [13] (3.22) [3], Et_3SnCN [14] (3.19) [3]. No certain examples of structural type III have as yet been substantiated. Six-coordinate triorganotin configurations are rare, nevertheless they have been postulated for some compounds. Barbieri and Stocco [15] claimed to have prepared the complex anion $Me_3SnCl_3^{2-}$, which exhibits a splitting of 3.49 mm sec^{-1} and thus

allowed these authors to prefer the *mer*-isomer IV to the *cis*-isomer V for which zero splitting would be expected.

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        R                      R
        |                      |
   R~   |   -X            R~   |   -X
     \  |  /                \  |  /
      `Sn´                   `Sn´
     /  |  \                /  |  \
   X´   |   `X           R´    |   `X
        |                      |
        R                      X

      (IV)                   (V)
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Barbieri and Herber [16] have also proposed a similar *mer*-six-coordinate structure for the trimethyltin chloride complex with bis(acetylacetone)ethylene-diimine. Both species readily dissociate in solution losing a chloride anion. Six-coordinate triorganotin species are always a possibility with potentially terdentate ligands. Ho and Zuckerman [17], however, in their comprehensive study of triorganotin derivatives of amino acids and dipeptides concluded that most of the derivatives contained four- or five-coordinate tin, but tricyclohexyltin glycyl-glycinate, with a splitting of 3.45 mm sec^{-1}, was considered also to possess a meridional structure.

In this paper we report data for a large number of triorganotin derivatives of potentially bidentate and terdentate substituted pyridines as possible models for a variety of configurations.
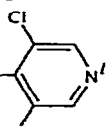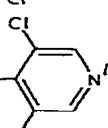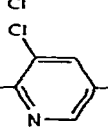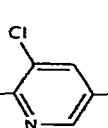
Results

Triorganotin derivatives of 2-pyridone (HOpy-2), 3-pyridone (HOpy-3), 2-thiopyridone (HSpy-2), 2-pyidyl aldehyde oxime (Hoximpy-2), 2-pyridyl-methanol (Halcpy-2), 2-pyridylcarboxylic acid (Hpic-2), 2,6-pyridyldicarboxylic acid (H$_2$dipic-2,6), and 8-hydroxyquinoline (Hoxin) were synthesised in essentially quantitative yield by the azeotropic dehydration of equimolecular quantities of the appropriate triorganotin oxide or hydroxide and the substituted pyridine in boiling benzene. The reaction of trimethyltin hydroxide with 2,6-pyridyldicarboxylic acid produced only the monotrimethyltin ester, whilst from the reaction with triphenyltin hydroxide only the distannyl ester was obtained no matter whether 1/1 or 1/2 molar ratios of reactants were used.

Tin-119m Mössbauer data

Mössbauer data for the compounds recorded at 77 K is listed in Table 1. The magnitude of the quadrupole splitting is clearly a function of the substituted-pyridyl ligand for the trialkyltin derivatives. Thus, the derivatives of 2-pyridone exhibit splittings in the range 3.21-3.38 mm sec^{-1}, derivatives of 3-pyridone in the range 3.10-3 22 mm sec^{-1}, 2-thiopyridone in the range 1.99-2.05 mm sec^{-1}, 2-pyridylaldehyde oxime 2.63(5)-2.81 mm sec^{-1}, 2-pyridylcarboxylic acid and 2,6-pyridyldicarboxylic acid 3.77-3.89(5) mm sec^{-1}. The corresponding triphenyltin derivatives have splittings usually some 0.2-0.3 mm sec^{-1} lower.

The values of the isomer shifts vary with the nature of the organic groups attached to tin as well as the substituted-pyridyl group. The isomer shifts of the

TABLE 1

TIN-119m MÖSSBAUER DATA

Compound	Isomeric shift (mm sec^{-1})	Quadrupole splitting (mm sec^{-1})
Me$_3$SnOpy-2	1.28	3.21
Et$_3$SnOpy-2	1.42	3.32
Pr$_3$SnOpy-2	1.44	3.38
Ph$_3$SnOpy-2	1.30	3.09
Me$_3$SnOpy-3	1.30	3.10
Et$_3$SnOpy-3	1.43	3.18
Pr$_3$SnOpy-3	1.41	3.22
Ph$_3$SnOpy-3	1.25	2.92
Me$_3$SnSpy-2	1.49	2.00
Et$_3$SnSpy-2 [a]	1.44	2.05
Pr$_3$SnSpy-2	1.43	1.99
Ph$_3$SnSpy-2 [b]	1.30	1.60
Me$_3$Snoximpy-2	1.30	2.81
Et$_3$Snoximpy-2	1.42	2.73(5)
Pr$_3$Snoximpy-2	1.43	2.63(5)
Me$_3$Snpic-2	1.37	3.89(5)
Et$_3$Snpic-2	1.49	3.83
Pr$_3$Snpic-2	1.49	3.88
Ph$_3$Snpic-2	1.29	3.49
Me$_3$Sndipic-2,6	1.36	3.77
(Ph$_3$Sn)$_2$dipic-2,6	1.30	3.36
Me$_3$Snalcpy-2	1.33	2.93
Me$_3$Snoxin	1.18	2 27
Ph$_3$Snoxin [c]	1.06	1.69
(C$_6$H$_{11}$)$_3$SnO$_2$CMe	1.69	3.27(5)
Me$_3$SnO$_2$CMe [d]	1.30	—3.68
Me$_4$N$^+$Me$_3$SnCl$_2$$^-$ [e]	1.27	—3.31
Me$_3$SnCl · C$_5$H$_5$N [f]	1.45	3.35
Me$_3$SnCl · Ph$_3$P=CHCOMe) [g]	1.29	3.44
Ph$_3$SnCl · (Ph$_3$P=CHCOMe) [g]	1.27	2.98
Me$_3$SnON=C$_6$H$_{10}$ [h]	1.43	2.96
Me$_3$SnONPhC(O)Ph [j]	1.34	2.36
Ph$_3$SnONPhC(O)Ph [j]	1.26	—1.94
Et$_4$N$^+$Me$_3$Snmnt$^-$ [k]	1.46	2.38
Et$_4$N$^+$Ph$_3$Snmnt$^-$ [k]	1.26	1.55
	1.51	3.77
	1.31	3.20
	1.56	2.86
	1.31	2.35

TABLE 1 (continued)

Compound	Isomeric shift (mm sec^{-1})	Quadrupole splitting (mm sec^{-1})
Et$_3$SnSpy-4 [l]	1.55	3.05
Ph$_3$SnSpy-4 [l]	1.37	2.61

[a] Lit. [19]: IS 1.56 mm/sec, QS 2.14 mm/sec. [b] Lit. [19]: IS 1.36 mm/sec, QS 1.58 mm/sec. [c] Lit. [24]: IS 1.04 mm/sec, QS −1.75 mm/sec. [d] Ref. 24. [e] Ref. 29. [f] Ref. 9. [g] Ref. 11. [h] Ref. 30. [j] Ref. 31. [k] Ref. 32. [l] Ref. 19.

trimethyltin derivatives of all the oxygen-containing ligands except Hoxin fall in the range 1.28-1.37 mm sec^{-1}, significantly lower than that of Me$_3$SnSpy-2 (1.49 mm sec^{-1}). The isomer shifts of the triethyltin and tripropyltin derivatives of 2- and 3-pyridone, 2-thiopyridone, and 2-pyridylaldehyde oxime all occur in the narrow range of 1.41-1.44 mm sec^{-1}, whilst the derivatives of 2-pyridylcarboxylic acid increase to 1.49 mm sec^{-1}. The triphenyltin derivatives, except again for the 8-hydroxyquinoline derivatives, have shifts in the range 1.25-1.30 mm sec^{-1}. The trimethyltin and triphenyltin derivatives of Hoxin both exhibit exceptionally low shifts of 1.18 and 1.06 mm sec^{-1}, respectively.

Agreement of the data for the compounds R$_3$SnSpy-2 (R = Et, Ph) and Ph$_3$Snoxin obtained in this study with previously recorded data was excellent.

^{1}H NMR data

The values of the Me—Sn proton chemical shifts and $^2J(^1H$—C—$^{119}Sn)$ are listed in Table 2. Apart from Me$_3$Snalcpy-2, which exhibits a chemical shift for the methyl protons of τ 9.71, again only a narrow range of values (τ 9.45-9.56) is observed. The magnitude of the coupling constant is also essentially indepen-

TABLE 2

Compound	τ(SnMe)	$^2J(^{119}Sn$—$^1H)$ (Hz)	ρ(SnMe) (cm^{-1})	ν(Sn—Me) (cm^{-1})
Me$_3$SnOpy-2	9.58	58.5	780vvs	507w, 516w, 538vs, 553vs
Me$_3$SnOpy-3	9.45	57.8	780vs	508mw, 517m, 545s, 577vs
Me$_3$SnSpy-2	9.51	57.2	775vs	512m, 532, 542ms
Me$_3$Snoximpy-2	9.49	57.2	780vvs	533ms sh, 549vvs
Me$_3$Snpic-2	9.49	59.0	787vs	538ms, 551s, 568m
Me$_3$Snalcpy-2	9.71$_5$	56.0	776vs	521s, 544s
Me$_3$Snoxin	9.56$_5$	56.2	790vvs	509vs, 521vs, 541vs
Me$_3$Sndipic-2,6	Insoluble		780vs	519mw, 542m, 552m, 562m
NEt$_4^+$Me$_3$SnCl$_2^-$ [a]		70.5		555vs
Me$_3$SnONPhC(O)Ph [b]	9.58	56.7		544, 524, 508
Me$_3$SnONHC(O)Ph [b]	9.62	56.7		540, 520, 501
Me$_3$SnON=C$_6$H$_{11}$ [c]	9.66	54.5		
Me$_3$SnON=CMe$_2$ [c]	9.62	57.2		

[a] Ref. 21. [b] Ref. 31. [c] Ref. 30.

dent of the nature of the substituted-pyridyl ligand and falls in the range 56.0-59.0 Hz.

Infrared data

Because of the complex distribution of vibrations associated with the pyridyl ring, it was not possible to assign all the observed bands in the spectra. However, some principal bands of interest are listed in Tables 3 and 4. All the trimethyltin derivatives exhibit an intense broad band at 775-790 cm^{-1}, which is readily assigned as ρ(Sn—Me). Bands which may reasonably be assigned as tin—carbon stretching modes in the spectra of the trimethyltin compounds are listed in Table 4. Ligand bands occurring in this region have been excluded by comparison with the corresponding triphenyltin derivatives in which the modes characteristic of principally metal—carbon stretching occur at much lower energy. Thus, whilst the Ph$_3$SnOpy-3, Ph$_3$SnSpy-2, and (Ph$_3$Sn)$_2$dipic-2,6 are clear between 500-600 cm^{-1}, Ph$_3$SnOpy-2 exhibits a ligand band at 533w cm^{-1} (corresponding to the band at 530m cm^{-1} in Me$_3$SnOpy-2). Similarly, the band at 523s in the spectrum of Me$_3$Snoximpy-2 occurs at 520m cm^{-1} in Ph$_3$Sn-oximpy-2, and the bands at 565vw and 588vw cm^{-1} in the spectrum of Me$_3$-Snoxin also occur at 577w and 595m cm^{-1} in Ph$_3$Snoxin. The ligand band at 532m cm^{-1} in Ph$_3$Snoxin is probably masked by the very strong tin—carbon stretching mode at 531 cm^{-1} in Me$_3$Snoxin.

The derivatives of the pyridylcarboxylic acids all show at least four intense overlapping bands which may be assigned to the $\nu_{antisym}$(OCO) vibration (Table 4). Although some fundamentals associated with the pyridyl ring will also occur in the same region, the spectra of the 2- and 3-pyridone and 2-thiopyridone derivatives show that these are usually much weaker in intensity (R$_3$SnOpy-2, two bands at ca. 1610s and ca. 1545m cm^{-1}; R$_3$SnOpy-3, two bands at ca. 1580m and ca. 1560m cm^{-1}; R$_3$SnSpy-2, two bands at ca. 1580m and ca. 1555 cm^{-1}) and are therefore probably masked in the spectra of the pyridylcarboxylic acid derivatives. The corresponding symmetric modes could not be assigned with certainty.

TABLE 3

CARBONYL STRETCHING FREQUENCIES FOR TRIORGANOTIN CARBOXYLATES (cm^{-1})

| Compound	ν(C=O) (cm^{-1})
Me$_3$Snpic-2	1598vvs, 1580vvs, 1562vvs, 1556vvs
Et$_3$Snpic-2	1619vvs, 1609vvs, 1593vvs, 1577vvs, 1567vvs
Pr$_3$Snpic-2	1609vs, 1596vvs, 1582vvs, 1563vvs, 1558vvs
Ph$_3$Snpic-2	1594vs, 1578s, 1570vs, 1546vvs
Me$_3$Sndipic-2,6	1655vvs, 1615vvs, 1588vvs, 1565vvs
(Ph$_3$Sn)$_2$dipic-2,6	1608vs, 1588vs, 1564vs, 1545s
(C$_6$H$_{11}$)$_3$SnO$_2$CMe	1648vvs [a]
(PhCH$_2$)$_3$SnO$_2$CMe [b]	1565
Me$_3$SnO$_2$CMe	1565 [c], 1576 [d]
Me$_3$Sn(glycinate) [e]	1630

[a] Ref. 17 gives ν(C=O), 1645 cm^{-1}. [b] Ref. 27. [c] Ref. 33. [d] Ref. 34. [e] Ref. 17.

TABLE 4

ANALYTICAL DATA

| Compound	M.p./B.p. (°C)/(°C/mm Hg)	Found (calcd.) (%)		
		C	H	N
Me₃SnOpy-2	165-167	37.29 (37.23)	5.28 (5.08)	5.32 (5.43)
Et₃SnOpy-2	100-102	43 81 (44.01)	6.09 (6.39)	4.25 (4.07)
Pr₃SnOpy-2	72-73	49.10 (49.14)	7.47 (7.37)	3.73 (4.09)
Ph₃SnOpy-2	129-130	62.41 (62.18)	4.68 (4.30)	2.80 (3.15)
Me₃SnOpy-3	175-177	37.36 (37.23)	5.33 (5.08)	5.15 (5.43)
Et₃SnOpy-3	110-111	44.12 (44.01)	6.58 (6.39)	4.99 (4.07)
Pr₃SnOpy-3	73-75	48.70 (49.14)	7.17 (7.37)	3.77 (4.09)
Ph₃SnOpy-3	200-202	61.81 (62.18)	4.57 (4.30)	2.71 (3.15)
Me₃SnSpy-2	70/0.01	35.04 (35.06)	5 00 (4.78)	5.35 (5.12)
Et₃SnSpy-2	91/0.07	42.45 (41.79)	6.00 (6.06)	4.75 (4.43)
Pr₃SnSpy-2	107/0.1	46.97 (46.94)	7.24 (7.04)	4.16 (3.91)
Ph₃SnSpy-2	100-102	60.60 (60.01)	4.59 (4.16)	2 87 (3.04)
Me₃Snoximpy-2	102/0.2	37.86 (37.92)	5.50 (4.95)	9.94 (9.84)
Et₃Snoximpy-2	100-101/0.4	44.71 (43.78)	6.44 (6.14)	9.10 (8.51)
Pr₃Snoximpy-2	106/0.03	48.48 (48.79)	7.89 (7.10)	7.20 (7.59)
Me₃Snpic-2	170 (dec.)	38.29 (37.78)	4.36 (4.55)	4.96 (4.86)
Et₃Snpic-2	142-143	44.69 (43.92)	6.16 (5.84)	4.03 (4.27)
Pr₃Snpic-2	143-145	48.32 (48.66)	7.02 (6.81)	3.45 (3.78)
Ph₃Snpic-2	168-167	61.49 (61.04)	4.39 (4.06)	2.75 (3.04)
Me₃Sndipic-2,6	270 (dec.)	35 88 (36.40)	3.73 (3.97)	3.83 (4.25)
(Ph₃Sn)₂dipic-2,6	132-134	58.16 (58.06)	3.98 (3.71)	2.24 (2.72)
Me₃Snalcpy-2	63-65	38.30 (39.74)	5.61 (5.56)	4.54 (5.15)
Me₃Snoxin	Oil	47.06 (46.78)	5.06 (4.91)	4.20 (4.55)
Ph₃Snoxin	147-148	65.12 (65 34)	4.29 (4.28)	2.64 (2.83)
(C₆H₁₁)₃SnO₂CMe	64-65	56.15 (56 21)	8.57 (8.50)	

Discussion

A priori, several modes of bonding exist for the triorganotin derivatives of the substituted pyridines under discussion. Four-coordination with tetrahedral-ly-coordinated tin (VI) is possible for all the derivatives if the substituted pyridyl residues function as unidentate ligands, but higher coordination numbers become possible if the pyridyl nitrogen takes part in coordination leading

(VI)   (VII)
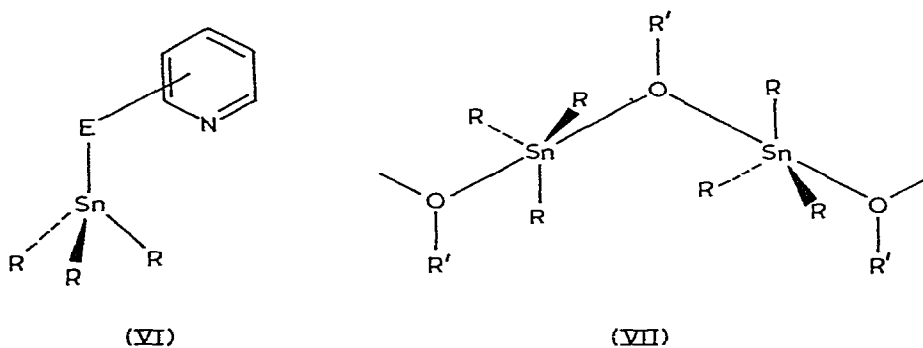
to five-coordinate structures such as I-III. Since carboxylate residues may function as bridging groups, six-coordinate structures such as IV and V are possible for the triorganotin derivatives of the pyridylcarboxylic acids. Extra coordination may also take place in the triorganotin derivatives of 2- and 3-pyridone, 2-pyridylaldehyde oxime, 2-pyridylalcohol, and 8-hydroxyquinoline, where the oxygen atom may function as a bridging group as in VII. Such a structural feature has previously been determined crystallographically for Me_3SnOMe [18] and $Me_3SnON=C_6H_{10}$ [1], and also in several other inorganic and organometallic tin derivatives [19]. The probability of similar sulphur bridging occurring in the derivatives of 2-thiopyridone is much less because of the much lower donor character of sulphur in such systems.

Derivatives of 2- and 3-pyridone

It might be expected that the 2-pyridonyl group would function as a chelating ligand and that the 3-pyridonyl group as a bridging bidentate ligand, giving rise to cis and trans five-coordinate structures I and II, respectively, for the triorganotin derivatives of these two ligands. Examination of the Mössbauer splitting data for the R_3SnOpy-2 derivatives, however, immediately rules out the cis configuration I, and further suggest the trans structure II for these compounds. Since it is sterically highly improbable that the 2-pyridonyl group is able to function as a bridging group, the remaining structural possibility for these derivatives is the oxygen-bridged chain structure VII, in which the pyridyl nitrogen takes no part in coordination. This structure is also a possibility for the R_3SnOpy-3 derivatives, although structure VIII involving nitrogen coordination may not be excluded. The quadrupole splittings of the triethyltin and triphenyltin derivatives of 3,5-dichloro-4-hydroxypyridine have values of 3.77 and 3.20 mm sec^{-1}, respectively, and most likely possess trans five-coordinate structures involving nitrogen coordination linking adjacent tin atoms, rather than oxygen bridging, due to the steric bulk of the two neighbouring chlorine atoms. The
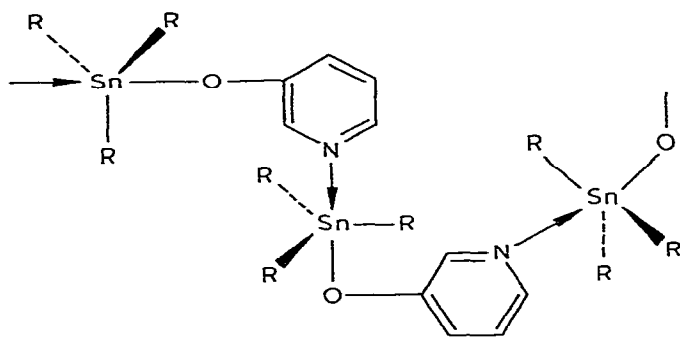
(VIII)

analogous derivatives of 3,5-dichloro-2-hydroxypyridine exhibit smaller split-tings of 2.86 (Et_3Sn) and 2.35 mm sec^{-1} (Ph_3Sn). Whereas the former value is not inconsistent with the oxygen-bridged *trans* structure VII in which the Et_3Sn unit deviates somewhat from planarity (i.e. the oxygen bridging is weakened due to the bulky chlorine substituents), the value of 2.35 mm sec^{-1} rules out such a structure for the triphenyltin derivative. It would seem that in this compound the chlorine substituents prevent the Ph_3Sn residue attaining planarity and force the *cis* five-coordinate structure to be adopted.

On the basis of "local" symmetry, group theory predicts two infrared active tin—carbon stretching modes ($A_1 + E$) for the four coordinate configuration VI, one (E') for the *trans* five-coordinate structure II, and three ($2A_1 + B_2$) for the *cis* five-coordinate structure I. Increasing deviation from planarity of the SnC_3 moiety in structure II will result in an increase in intensity of the infrared inactive $D_{3h}A_1$ mode. Thus, in cyclohexane solution Me_3SnCl exhibits two modes at 542 and 513 cm^{-1} [20], whilst *trans*-$Me_3SnCl_2^-$ exhibits only a single very strong band at 555 cm^{-1} [21]. $Me_3SnONPhC(O)Ph$, which almost certainly possesses the *cis* structure I deduced crystallographically for the tri-phenyltin homologue [5], exhibits three bands of similar intensity at 544, 524, and 508 cm^{-1} [7].

Both $Me_3SnOpy-2$ and $Me_3SnOpy-3$ exhibit four bands which may be assigned as tin—carbon stretching modes. From the Mössbauer data, however, only a single band is expected for each compound. This apparent disparity may be rationalised if two different molecular units occur in the unit cell of the crystal, in which case the two bands at higher energy may be assigned as antisymmetric Sn—C stretching modes, and the two weak bands as the corresponding symmetric modes of nearly planar $SnMe_3$ moieties.

Derivatives of 2-thiopyridone

The trialkyltin derivatives of 2-thiopyridone are all mobile oils indicating the probable absence of bridging in these compounds, and indeed the quadru-pole splitting values are much lower (1.99-2.05 mm sec^{-1}) than those of the corresponding oxygen compounds. That of $Ph_3SnSpy-2$ is only 1.60 mm sec^{-1}. In contrast, the observed splittings for $Et_3SnSpy-4$ and $Ph_3SnSpy-4$ are 3.05 and 2.61 mm sec^{-1}, respectively, and in addition the latter compound is known

to possess a solid-state structure similar to VIII in which the pyridyl nitrogen coordinates to an adjacent tin atom forming a coordinate polymeric structure containing planar Ph_3Sn units [22]. Thus, the quadrupole splitting values of the R_3SnSpy-2 derivatives indicate either the four-coordinate structure VI or the *cis* five-coordinate structure I. The infrared spectrum of Me_3SnSpy-2, however, exhibits three bands of moderate intensity in the tin—carbon stretching region consistent with the *cis* five-coordinate structure I, which is also presumably adopted by the higher homologues.

Derivatives of 8-hydroxyquinoline

The oxine group is known from crystallographic data to function as a chelating ligand towards tin in $Me_2Sn(oxin)_2$ [23], and Sams et al. have interpreted the magnetically perturbed Mössbauer spectrum of $Ph_3Snoxin$ in terms of the *cis* five-coordinate structure I [24]. The quadrupole splittings for this compound (1.69 mm sec^{-1}) and $Me_3Snoxin$ (2.27 mm sec^{-1}) are similar to those previously measured for the hydroxamic acid derivatives $Me_3SnONPhC(O)$-Ph (2.36 m sec^{-1}) and $Ph_3SnONPhC(O)Ph$ (—1.94 mm sec^{-1}) [7], which is one of the only two crystallographically-confirmed examples of the *cis* geometry I. Infrared data lend further support to the assignment of structure I to the R_3-Snoxin derivatives, since the spectrum of $Me_3Snoxin$ exhibits three tin—carbon stretching modes at 509, 521, and 541 cm^{-1}, as do Me_3SnSpy-2 and $Me_3SnONPh$-C(O)Ph (R = H, Ph).

Derivatives of 2-pyridylmethanol and 2-pyridylaldehyde oxime

Although the geometry of the 2-pyridylmethoxide ligand is very similar to the oxime ligand which functions as a chelating ligand, the quadrupole splittings of the 2-pyridylmethanol and 2-pyridylaldehyde oxime derivatives fall in the range 2.63(5)-2.93 mm sec^{-1}, and are therefore intermediate between that expected for the *trans* five-coordinate geometry II and the *cis* five-coordinate geometry I or the four-coordinate structure VI. Configurations I and VI may therefore be ruled out, and the lower splittings observed must arise from deviations from the ideal *trans* geometry II such that the C—Sn—C bond angles of the SnC_3 unit progressively decrease as the coordinate bond E···Sn becomes longer, giving rise to the distorted *trans* geometry IX at the tin atoms. Whether the
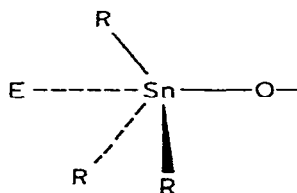
(IX)

extra coordination arises from bridging-oxygen or pyridyl-nitrogen atoms is indeterminate in the absence of diffraction data. The progressive decrease in the magnitude of the quadrupole splitting of the $R_3Snoximpy$-2 derivatives as the alkyl group becomes larger (Me, 2.81; Et, 2.73(5); Pr, 2.63(5)) is in the direction expected for the proposed model. In both Me_3SnOMe [18] and Me_3Sn-

ON=C_6H_{10} [1] the oxygen atoms bridge adjacent Me_3Sn units, the nitrogen atom in the latter compound not participating in coordination to tin, and so a similar chain structure as VII, but distorted from "local" D_{3h} symmetry as in IX, is proposed for these derivatives. Further, it may be concluded that the deviation of the C_3Sn moiety from planarity increases in the order $Me_3Snalcpy-2$ < $Me_3Snoximpy-2$ < $Et_3Snoximpy-2$ < $Pr_3Snoximpy-2$.

Both $Me_3Snoximpy-2$ and $Me_3Snalcpy-2$ are mobile oils at room temperature, and therefore probably not associated under those conditions but rather exist as the four-coordinate or *cis* five-coordinate structures VI or I. Thus, the observation of two strong tin—carbon stretching bands at 549vs, 533ms and 544s, 521s cm^{-1}, respectively, for the two compounds at room temperature is not inconsistent with the associated structure deduced from the Mössbauer data in the solid at 77 K.

Derivatives at 2-pyridylcarboxylic acid and 2,6-pyridyldicarboxylic acid

The 2-pyridylcarboxyl group is potentially a terdentate ligand since the carbonyl group may function as a bridging group as in Me_3SnO_2CMe [25], $Me_3SnO_2CF_3$ [25], and $(PhCH_2)_3SnO_2CMe$ [26]. However, the acetate group is unidentate in $(C_6H_{10})_3SnO_2Me$ [27]. Whether or not the carboxylate residue functions as a bidentate group is apparent from the position of the antisymmetric (OCO) stretching vibration in the infrared. These bands for the triorganotin pyridylcarboxylates and also for model compounds are listed in Table 3. In $(C_6H_{10})_3SnO_2CMe$ this vibration occurs as an intense band at 1648 cm^{-1}, whilst in $Me_3Sn(glycylglycinate)$ [17], in which glycinate groups bridge adjacent tin atoms via nitrogen [28], the band is found at 1630 cm^{-1}. The two compounds which contain bridging acetate groups, R_3SnO_2CMe (R = Me, $PhCH_2$), exhibit bands at ca. 70 cm^{-1} lower energy at 1565-1576 cm^{-1}. The spectra of the $R_3Snpic-2$ derivatives all exhibit several intense bands in the region 1546-1619 cm^{-1}, indicating that in these compounds, both oxygen atoms of the 2-pyridylcarboxyl group are bonded to tin atoms. Similarly, in $(Ph_3Sn)_2dipic-2,6$, which exhibits ν_a(OCO) bands in the range 1545-1608 cm^{-1}, all four oxygens participate in coordination to tin. However, the monoester, $Me_3Sndipic-2,6$, exhibits three bands at 1565, 1588, and 1615 cm^{-1} assignable to coordinating oxygen atoms of carboxyl groups, and also a band at 1655 cm^{-1} due to a "free" uncoordinated carbonyl group.

In Me_3SnO_2CMe, $Me_3SnO_2CCF_3$, and $(PhCH_2)_3SnO_2CMe$, carboxylate groups bridge trigonal planar SnC_3 units. If a similar situation prevailed in the present case, with the pyridyl nitrogen atoms not participating in coordination, only a single tin—carbon stretching mode would be observed in the infrared. However, both trimethyltin derivatives exhibit multiple tin—carbon stretching modes indicative of the *cis* or *mer* five-coordinate geometries, I or III, or the analogous six-coordinate geometries, IV or V.

The magnitude of the Mössbauer quadrupole splittings observed for these derivatives (3.77-3.895 mm sec^{-1} for the trialkyltin derivatives, 3.36 and 3.49 mm sec^{-1} for the triphenyltin derivatives) immediately excludes two *cis* geometries, for which values of ca. 1.7-2.3 mm sec^{-1} (for I) and 0 (for V) are expected, but are consistent with the meridional geometries III and V. An unequivocal choice between the five- and six-coordinate geometries is not possible in

the absence of crystal data, and the occurrence of which depends on the participation or otherwise in coordination of the pyridyl-nitrogen atom. If, however, the nitrogen atom does not take part in coordination, it might be expected that the *trans* rather than the *mer* five-coordinate stereochemistry with planar C_3Sn units of D_{3h} "local" symmetry would be adopted as in the known crystallographic examples of bridged triorganotin carboxylates. We therefore propose that the $R_3Snpic-2$ derivatives possess the *mer* six-coordinate geometry.

The interpretation of geometry from Mössbauer quadrupole splitting data alone should be approached with caution. This is demonstrated by the data for $(C_6H_{11})_3SnO_2CMe$, which has four-coordinated tin atoms in a distorted tetrahedral arrangement with unidentate acetate groups [27]. The quadrupole splitting is, however, 3.27(5) mm sec^{-1} a value characteristic of the *trans* five-coordinate geometry II, much larger than that expected for a four-coordinate R_3SnO^- species, and arises from the greater electronegativity of the carboxylate residue.

^{1}H NMR data

The two-bond $^2J(^1H-C-^{119}Sn)$ coupling constant in methyltin compounds is a guide, via the Fermi contact mechanism, to the distribution of tin 5s electron density in the valence shell. For Me_4Sn, which has T_d symmetry and therefore 25% s character per Sn$-$C bond, the value of the coupling constant is 54 Hz. Replacement of one methyl group by an electronegative group results in the preferential concentration of s character in the Sn$-$C bonds, and therefore the coupling constant rises ($Me_3SnON=C_6H_{10}$, 54.5 Hz; $Me_3SnON=CMe_2$, 57.2 Hz). This effect is much greater in compounds with the *trans*-R_3SnX_2 configuration, which exhibit values of ca. 70 Hz [21]. Compounds possessing the *cis*-R_3SnX_2 geometry exhibit values similar to those observed for four-coordinate Me_3SnX.

The data for the trimethyltin derivatives under discussion here are listed in Table 2. The values are remarkably constant and fall in the narrow range 56.0-59.0 Hz. It is immediately apparent that any intermolecular association leading to *trans* five-coordinate structures is destroyed upon dissolution. Thus, in solution all the derivatives must possess the four-coordinate VI or *cis* five-coordinate III structures. Since the 3-pyridonyl ligand cannot function as a chelating ligand, $Me_3SnOPy-3$ must therefore contain four-coordinated tin. A choice between the two possible geometries for the remaining compounds is not possible from the present data, although no doubt the *cis* five-coordinate structure deduced for $Me_3SnSpy-2$ and $Me_3Snoxin$ in the neat liquids is preserved in solution. In the other cases, it is highly probable that the destruction of the solid-state intermolecular association upon dissolution is accompanied by a *trans*-$Me_3SnX_2 \rightarrow$ *cis*-Me_3SnX_2 structural rearrangement.

Experimental

Most of the complexes were air stable and therefore could be handled without any precaution. The derivatives of 2-pyridylaldehyde oxime and 2-pyridylmethanol hydrolysed readily in air and so were handled under an atmosphere of dry nitrogen.

Infrared spectra were recorded using a Perkin—Elmer 521 spectrophoto-

meter calibrated using water vapour and ammonia. ^{1}H NMR data were obtained using a Varian HA-100 spectrometer using TMS as an internal lock signal. Samples for examination were prepared by dissolution in $CDCl_3$. Tin-119m Mössbauer spectra were obtained at 77 K using a Harwell spectrometer equipped with a 256 multichannel analyser against a $Ba^{119m}SnO_3$ source. Data reduction to Lorentzian line shapes was effected by usual least squares methods.

Preparation of the complexes

The synthesis of all the complexes was very similar. In general, the triorgano-tin hydroxide or bis(triorganotin) oxide and the protic substituted pyridine were mixed in benzene and water removed azeotropically using a Dean and Stark apparatus. After all the water had been removed from the reaction mixture, the solvent was removed in vacuo, and the resultant material either distilled or re-crystallised. Essential physical and analytical data are presented in Table 4.

Acknowledgement

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